

841. Complexes of Transition Metals with a Tetra-tertiary Arsine.

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The tetra-tertiary arsine $\text{As}(\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{AsMe}_2)_3$ has been synthesised, and its complexes with salts of iron(II), iron(III), cobalt(III), nickel(II), and nickel(III) have been studied. The magnetic moments of these compounds indicate that in all cases the metal atom is spin-paired. The derivatives of the bivalent metals are six-covalent non-electrolytes of the type $[\text{M ttaX}_2]$; the trivalent derivatives are salts $[\text{M ttaX}_2]\text{Y}$ (tta = tetra-tertiary arsine).

The instability of the cobalt(II) and nickel(II) compounds is noteworthy.

In a previous paper we described cobalt complexes with a terdentate amine, 2,2'-diamino-diethylamine, and with a quadridentate amine, 2,2',2''-triaminotriethylamine.¹ The complexes with the terdentate ligand have been compared with the corresponding derivatives of a tritertiary arsine $\text{Me}\cdot\text{As}(\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{AsMe})_2$.² The present paper describes the preparation of a tetra-tertiary arsine, tris-(3-dimethylarsinylpropyl)arsine, $\text{As}(\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{AsMe}_2)_3$, and some of its metallic derivatives.

The tetra-tertiary arsine has four arsenic atoms available for co-ordination to the same metal atom. Models show that the arsine should be able to co-ordinate readily if the metal uses tetrahedral or octahedral bonding orbitals, but not if the bonds are square-planar.

Ligand-field theory indicates that when a metal in the latter half of the first transition series forms complexes with highly polarisable ligands (e.g., tertiary arsines) then electron-pairing should occur in the $3d_{\epsilon}$ -orbitals, giving the non-bonding configurations shown in Table 1. Consequently, for iron(II), iron(III), cobalt(III), and nickel(IV), where the $3d_{\gamma}$ -

TABLE 1.

Metal and valency	Confign.	No. of unpaired electrons	Metal and valency	Confign.	No. of unpaired electrons
Iron(II)	$(3d_{\epsilon})^6$	0	Nickel(II)	$(3d_{\epsilon})^6(3d_{\gamma})^2$	0*
Iron(III)	$(3d_{\epsilon})^5$	1	Nickel(III)	$(3d_{\epsilon})^6(3d_{\gamma})^1$	1
Cobalt(II)	$(3d_{\epsilon})^6(3d_{\gamma})^1$	1	Nickel(IV)	$(3d_{\epsilon})^6$	0
Cobalt(III)	$(3d_{\epsilon})^6$	0			

* See text.

orbitals are not occupied by non-bonding electrons, regular octahedral derivatives would be expected. However, in cobalt(II), nickel(II), and nickel(III), the $3d_{\gamma}$ -orbitals are occupied by one or two electrons. These electrons, which occupy the $3d_{z^2}$ -orbital, will repel the ligands in the *trans*-positions. The resultant stereochemistry will be either that of a distorted octahedron with two long *trans*-bonds, or, if the repulsion is sufficiently high, that of a square plane.³ The $3d_{z^2}$ -orbital will be in a fairly high ligand field compared with the $3d_{\epsilon}$ -orbitals which point between the ligand directions. Consequently, electrons in the former orbital will be less firmly bound than the other non-bonding electrons and might be expected to be lost quite readily.

Summarising, it is predicted that the metal complexes of the tetra-arsine should be spin-paired and octahedral, and that the cobalt(II) and nickel(II) compounds should be fairly readily oxidised to the corresponding cobalt(III), and nickel(III) and nickel(IV) compounds.

The complexes of the tetra-arsine (tta) that we isolated, together with the complete magnetic data, are summarised in Table 2.

¹ Barclay and Barnard, *J.*, 1958, 2540.

² Barclay and Nyholm, *Chem. and Ind.*, 1953, 378; Barclay, *Rev. Pure Appl. Chem. (Australia)*, 1954, 4, 77.

³ Orgel, "Introduction to Transition Metal Chemistry," Methuen, London, 1960, p. 63.

The ligand itself was synthesised by the reactions, $\text{HO}\cdot[\text{CH}_2]_3\cdot\text{OH} (+ \text{S}_2\text{Cl}_2) \longrightarrow \text{HO}\cdot[\text{CH}_2]_3\cdot\text{Cl} (+ \text{Na}_2\text{AsO}_3) \longrightarrow \text{HO}\cdot[\text{CH}_2]_3\cdot\text{AsO}_3\text{H}_2 (+ \text{SO}_2 + \text{HCl} + \text{SOCl}_2) \longrightarrow \text{Cl}\cdot[\text{CH}_2]_3\cdot\text{AsCl}_2 (+ \text{MeMgI}) \longrightarrow \text{Cl}\cdot[\text{CH}_2]_3\cdot\text{AsMe}_2$ (Grignard + AsCl_3) \longrightarrow As ($[\text{CH}_2]_3\cdot\text{AsMe}_2$)₃. The product was a white wax, melting at $\sim 23^\circ$, which, in contrast with simpler arsines, was not readily oxidised in air.

TABLE 2.
Magnetic susceptibilities of powdered samples at 20° .

Complex	Colour	$10^6\chi_M$	10^6D^*	$10^6\chi'_M$	μ (B.M.)
Fe tta(SCN) ₂	Purple	—†	—	—	0.0
Fe ttaCl ₂ FeCl ₄	Red	16,260	488	16,748	4.45
Co ttaCl ₂ ClO ₄	Green	—†	—	—	0.0
Co ttaBr ₂ Br	Brown	—†	—	—	0.0
Co ttaBr ₂ ClO ₄	Brown	—†	—	—	0.0
Co ttaI ₂ I	Brown	—†	—	—	0.0
Ni ttaI ₂	Blue	—†	—	—	0.0
Ni ttaCl ₂ ClO ₄	Purple	1190	440	1630	1.96
Ni ttaBr ₂ Br	Purple	1200	463	1663	1.98
Ni ttaBr ₂ ClO ₄	Blue	1150	461	1611	1.95
Ni ttaI ₂ I	Green	1040	507	1597	1.94

* These values of the diamagnetic correction D are calculated from the constants given by Selwood⁴; the diamagnetism of the metal atom has been ignored in all cases.

† The method of measurement did not permit precise determination of diamagnetic susceptibilities.

The purple diamagnetic iron(II) compound Fe tta(SCN)₂ is a non-electrolyte in nitrobenzene. It can therefore be formulated as a spin-paired octahedral complex, with *cis*-thioanato-groups.

The complex Fe ttaCl₂FeCl₄ has an effective magnetic moment of 4.45 B.M. per iron atom, intermediate between the values expected for three and four unpaired electrons. Nyholm⁵ has pointed out that this situation may arise when a compound contains two metal atoms, one with a spin-free configuration, and the other spin-paired. Here, by analogy with the corresponding diarsine compound, it is probable that the anion is the tetrachloroferrate(III) ion. By subtracting the known susceptibility of this anion from the total, the susceptibility of the complex cation can be calculated:

	$10^6\chi_M$	10^6D	$10^6\chi'_M$	μ (B.M.)
Fe ttaCl ₂ FeCl ₄	16,260	488	16,748	4.45 per Fe
[FeCl ₄] ⁻	15,060	94	15,154	5.98
[Fe ttaCl ₂] ⁺	1200	394	1594	1.95

i.e., the cation is best formulated with a spin-paired octahedral configuration. This implies that the compound is a uni-univalent electrolyte, which is confirmed by the observed molar conductivity in nitrobenzene. Attempts to prepare the perchlorate salt of this cation led to decomposition.

In spite of numerous precautions to exclude oxidising agents, it was impossible to isolate a cobalt(II) complex. The cobalt(III) compounds are all diamagnetic uni-univalent electrolytes of the type [Co ttaX₂]Y, a configuration supported by preparation of the dichloro- and the dibromo-perchlorate (X = Cl, Br; Y = ClO₄).

Similarly the complexes of nickel(II) proved difficult to prepare. In only one case, by using nickel iodide in an atmosphere of nitrogen, could such a compound be isolated. This dark blue di-iodide is diamagnetic and a non-electrolyte in nitrobenzene, and is formulated with a spin-paired octahedral configuration. The deeply coloured nickel(III) complex salts all have magnetic moments corresponding to one unpaired electron and are uni-univalent electrolytes in nitrobenzene. They are undoubtedly spin-paired octahedral

⁴ Selwood, "Magnetochemistry," Interscience Publ., Inc., New York, 1956, 2nd edn., p. 91.

⁵ Nyholm, *J.*, 1950, 851.

salts of the type $[\text{Ni ttaX}_2]\text{Y}$. This view is substantiated by isolation of the perchlorates $[\text{Ni ttaX}_2]\text{ClO}_4$ ($\text{X} = \text{Cl}, \text{Br}$). Attempts to obtain Ni(IV) compounds, which should be possible by removal of the single electron in the $3d_{z^2}$ -orbital of a nickel(III) atom, proved unsuccessful: the oxidising agents (dilute nitric acid, chlorine, or ceric sulphate) caused the decomposition of the complex. With ^{15}N -nitric acid a deep red solution was obtained initially, but this rapidly decomposed to give the green solution characteristic of the nickel(II) ion.

Consequently, in all cases investigated, a spin-paired octahedral configuration is believed to occur. In each case there are four metal-arsenic bonds and two metal-halogen or metal-thiocyanate bonds in *cis*-positions. However, covalent bonding between a metal atom and a perchlorate ion would not be expected, owing to the very low polarisability of the latter, and a different type of tetra-arsine complex should therefore arise. When alcoholic solutions of nickel perchlorate and the tetra-arsine are mixed a bright purple precipitate separates immediately. A similar precipitate is also obtained when any nickel tetra-arsine complex is treated with dilute perchloric acid or aqueous sodium perchlorate. This compound is insoluble in all the common solvents, precluding conductivity and molecular-weight measurements. It is diamagnetic, and the metal is therefore presumably bivalent. Analyses show that the composition varies from preparation to preparation, the results not fitting any reasonable formulation. These facts make it likely that the compound is polymerised by the sharing of tetra-arsine groups between different nickel atoms, in such a way that each becomes octahedrally co-ordinated by six arsenic atoms. It is interesting that Barclay and Nyholm² could not obtain a pure complex of nickel perchlorate with the tri-tertiary arsine. They attributed this to partial oxidation, but an alternative explanation is that the compound is polymeric, similarly to the tetra-arsine complex.

EXPERIMENTAL

Tris-(3,3',3''-dimethylarsinylpropyl)arsine ("tetra-arsine").—This preparation took place in a number of stages. First, trimethylene chlorohydrin was converted into dichloro-3-chloropropylarsine by the methods of Gough and King;⁶ then 3-chloropropyl dimethylarsine was prepared in the following manner:⁷ A Grignard reagent, from methyl iodide (142 g.) and magnesium (24 g.), was filtered through glass wool and added slowly to a solution of dichloro-3-chloropropylarsine (100 g.) in dry ether (250 ml.). The whole was agitated by a stream of dry nitrogen during the addition and all subsequent operations. A vigorous reaction occurred, and initially a yellow solid separated, but eventually most of this disappeared, two layers being formed. After the final addition the mixture was refluxed for 10 min. and the complex decomposed by addition of ammonium chloride solution. The ethereal layer was separated and washed successively with water, saturated sodium hydrogen carbonate solution, and again with water. After drying (MgSO_4), the ether was removed and the residue distilled under reduced pressure in an atmosphere of coal gas. 3-Chloropropyl dimethylarsine (65 g.), b. p. $60\text{--}62^\circ/10\text{ mm.}$, was obtained as a colourless oil with a garlic odour.

Magnesium (10 g.) was covered with dry ether and a Grignard reaction started with a little methyl iodide. When the reaction was proceeding vigorously, 3-chloropropyl dimethylarsine (65 g.) in dry ether (150 ml.) was added at such a rate as to keep the ether boiling. Then the mixture was refluxed for 15 min., cooled, and decanted through glass wool to remove the excess of magnesium, and arsenic trichloride (22 g.) in ether (60 ml.) was slowly added. Large quantities of a yellow solid were formed. The mixture was refluxed for 30 min., then the complex was decomposed with ammonium chloride solution, and the ethereal layer was separated, washed with sodium hydroxide solution and water, and dried (MgSO_4). The ether was distilled off and the remaining oil heated at $120^\circ/3\text{--}4\text{ mm.}$ until all volatile matter was removed. The residue was cooled in solid carbon dioxide-alcohol, the *tetra-arsine* separating as a greasy white solid, m. p. $\sim 23^\circ$. It was recrystallised from methanol (Found: C, 34.85; H, 7.05. $\text{C}_{15}\text{H}_{36}\text{As}_4$ requires C, 34.9; H, 7.05%).

⁶ Gough and King, *J.*, 1928, 2439.

⁷ Barclay and Nyholm, unpublished observations.

4272 *Complexes of Transition Metals with a Tetra-tertiary Arsine.*

Dithiocyanato(tetra-arsine)iron(II).—Anhydrous ferric chloride (0.15 g.) was dissolved in ethanol (10 ml.), and the solution filtered, and treated with ammonium thiocyanate (0.28 g.) in ethanol (10 ml.). Tetra-arsine (0.5 g.) in warm ethanol (10 ml.) was added to the deep red solution. A dark brown precipitate rapidly separated and was set aside for 5 min. before collection. The filtrate was left overnight, small deep purple crystals being produced. This *complex* (0.3 g.) was recrystallised from ethanol (Found: C, 29.8; H, 5.35; Fe, 8.3. $C_{17}H_{36}As_4FeN_2S_2$ requires C, 29.65; H, 5.3; Fe, 8.1%); it had molecular conductivity ($9.3 \times 10^{-4}M$ -solution in nitrobenzene) at $20^\circ = 2.5$ mho.

Dichloro(tetra-arsine)iron(III) Tetrachloroferrate(III).—Anhydrous ferric chloride (0.15 g.) was dissolved in ethanol (10 ml.), filtered, and added with vigorous stirring to a solution of tetra-arsine (0.5 g.) in ethanol (10 ml.). A brick-red precipitate was immediately formed and after 5 min. was filtered off and washed with ethanol in which it was only slightly soluble. The *complex* (0.4 g.) was dried in a vacuum-desiccator (Found: C, 21.6; H, 4.2; Fe, 13.2. $C_{15}H_{36}As_4Cl_6Fe_2$ requires C, 21.45; H, 4.3; Fe, 13.3%). Its molecular conductivity in $1.65 \times 10^{-3}M$ -solution in nitrobenzene at 20° was 19.0 mho.

Dichloro(tetra-arsine)cobalt(III) Perchlorate.—Ethanolic solutions containing cobalt chloride hexahydrate (0.5 g.) and sodium perchlorate (0.35 g.) were mixed, filtered, and added to a solution of tetra-arsine (1.1 g.) in warm ethanol (20 ml.). The blue solution became deep red and an olive-green precipitate was produced. The *perchlorate* (0.6 g.) was filtered off and dried in a vacuum-desiccator [Found: C, 23.9; H, 4.8; Cl (not perchlorate), 9.6. $C_{15}H_{36}As_4Cl_3CoO_4$ requires C, 24.15; H, 4.9; Cl (not perchlorate), 9.6%]. The molecular conductivity in $2.6 \times 10^{-3}M$ -solution in nitrobenzene at 20° was 25.0 mho.

Dibromo(tetra-arsine)cobalt(III) Bromide.—Cobalt bromide hexahydrate (0.3 g.) and lithium bromide (0.1 g.) in alcohol were mixed and added to a warm alcoholic solution of the tetra-arsine (0.45 g.). The brown solution was evaporated to dryness at room temperature. The complex was extracted from the excess of lithium bromide with chloroform, and this solution was treated at the b. p. with high-boiling light petroleum. On cooling, dark brown needles of the *bromide* (0.4 g.) were obtained (Found: C, 22.0; H, 4.4; Br, 29.4. $C_{15}H_{36}As_4Br_3Co$ requires C, 22.1; H, 4.45; Br, 29.4%); the molecular conductivity in $1.6 \times 10^{-3}M$ -solution in nitrobenzene at 20° was 22 mho.

Dibromo(tetra-arsine)cobalt(III) Perchlorate.—Alcoholic solutions of cobalt bromide hexahydrate (0.7 g.) and sodium perchlorate (0.3 g.) were mixed, filtered, and added to a warm alcoholic solution of the tetra-arsine (1.0 g.). A khaki-brown precipitate of the *perchlorate* (0.7 g.) was rapidly produced (Found: C, 21.3; H, 4.2; Br, 19.1. $C_{15}H_{36}As_4Br_2ClCoO_4$ requires C, 21.6; H, 4.2; Br, 19.1%). The molecular conductivity in $1.4 \times 10^{-3}M$ -solution in nitrobenzene at 20° was 21 mho.

Di-iodo(tetra-arsine)cobalt(III) Iodide.—Cobalt chloride hexahydrate (0.2 g.) and lithium iodide (0.8 g.) in alcohol were mixed and added to a warm alcoholic solution of the tetra-arsine (0.4 g.). On evaporation of the red-brown solution a deep-brown oil was obtained. This crystallised from chloroform–light petroleum, giving the dark brown *iodide* (0.4 g.) (Found: C, 18.7; H, 3.5; I, 39.75. $C_{15}H_{36}As_4CoI_3$ requires C, 18.8; H, 3.8; I, 39.9%), whose molecular conductivity in $1.3 \times 10^{-3}M$ -solution in nitrobenzene at 20° was 23 mho.

Di-iodo(tetra-arsine)nickel(II).—A solution of nickel iodide (0.3 g.) in alcohol was boiled free from dissolved air and saturated with coal gas. The tetra-arsine (0.5 g.) in air-free alcohol was rapidly added and the deep blue solution vigorously shaken. It was concentrated in a vacuum-desiccator and filtered in an atmosphere of coal gas. Deep blue crystals of the *complex* (0.4 g.) were obtained (Found: C, 21.6; H, 4.5; Ni, 7.0. $C_{15}H_{36}As_4I_2Ni$ requires C, 21.75; H, 4.4; Ni, 7.1%), whose molecular conductivity in $1.4 \times 10^{-3}M$ -solution in nitrobenzene at 20° was 5.1 mho.

Dichloro(tetra-arsine)nickel(III) Perchlorate.—This compound was prepared after attempts to isolate the trichloride had yielded only deep blue oils. Nickel chloride hexahydrate (0.2 g.) and sodium perchlorate (0.13 g.) in alcohol were mixed and added to a warm alcoholic solution of the tetra-arsine (0.45 g.). The deep blue solution, which almost immediately began to deposit purple crystals, was set aside overnight. The deep purple *perchlorate* (0.5 g.) was filtered off and dried in a vacuum-desiccator [Found: C, 23.9; H, 4.7; Cl (not perchlorate), 9.7; Ni, 7.8. $C_{15}H_{36}As_4Cl_3NiO_4$ requires C, 24.2; H, 4.9; Cl (not perchlorate), 9.6; Ni, 7.9%]. The molecular conductivity in $2.0 \times 10^{-3}M$ -solution in nitrobenzene at 20° was 25.0 mho.

Dibromo(tetra-arsine)nickel(III) Bromide.—The tetra-arsine (0.8 g.) in warm alcohol was added to a filtered alcoholic solution containing nickel chloride hexahydrate (0.4 g.) and lithium

bromide (1.0 g.). The deep blue solution was evaporated at room temperature to a blue oil which crystallised from chloroform–light petroleum, giving the dark purple *bromide* (0.35 g.) (Found: C, 22.1; H, 4.35; Br, 29.5; Ni, 7.1. $C_{15}H_{36}As_4Br_3Ni$ requires C, 22.15; H, 4.5; Br, 29.45; Ni, 7.2%). The molecular conductivity in $1.6 \times 10^{-3}M$ -solution in nitrobenzene at 20° was 25.0 mho.

Dibromo(tetra-arsine)nickel(III) Perchlorate.—A filtered alcoholic solution containing nickel bromide trihydrate (0.15 g.) and sodium perchlorate (0.07 g.) was added to a warm alcoholic solution of the tetra-arsine (0.26 g.). Deep blue crystals of the *perchlorate* (0.4 g.) were rapidly formed (Found: C, 21.8; H, 4.5; Br, 19.0; Ni, 6.9. $C_{15}H_{36}As_4Br_2ClNiO_4$ requires C, 21.6; H, 4.35; Br, 19.35; Ni, 7.0%). The molecular conductivity in $9.1 \times 10^{-4}M$ -solution in nitrobenzene at 20° was 29.0 mho.

Di-iodo(tetra-arsine)nickel(III) Iodide.—The tetra-arsine (0.6 g.) in warm alcohol was added to a filtered alcoholic solution containing nickel chloride hexahydrate (0.3 g.) and lithium iodide (1.2 g.). The deep green solution was concentrated under reduced pressure, very dark green crystals of the *iodide* (0.3 g.) being obtained (Found: C, 18.7; H, 3.6; I, 39.8; Ni, 6.2. $C_{15}H_{36}As_4I_3Ni$ requires C, 18.8; H, 3.8; I, 39.9; Ni, 6.1%). The molecular conductivity in $1.6 \times 10^{-3}M$ -solution in nitrobenzene at 20° was 25.0 mho.

Magnetic Measurements.—The magnetic susceptibilities were determined for the finely powdered solids (*ca.* 10 mg.) in an apparatus of the type described by Blaha.⁸

Conductivity Measurements.—A conductance bridge with a dip-type cell was used. It has been shown⁹ that the molar conductivity of a uni-univalent electrolyte in nitrobenzene solution at room temperature is about 20–25 mho.

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⁸ Blaha, *Mikrochem.*, 1952, **39**, 339.

⁹ Ali, Brewer, Chadwick, and Garton, *J. Inorg. Nuclear Chem.*, 1959, **9**, 130, and references therein.